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Manganese Segregation on Defects of a GaSb Crystall Lattice

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Abstract: **When doping gallium antimonide with 2 at.% Mn, it was found that, as a result of quenching of the melt, manganese segregates on grain-forming dislocations of the crystalline GaSb (111) texture in the form of microinclusions based on the ferromagnetic compound MnSb. Manganese atoms segregate on GaSb dislocations discretely with periodic spacing of inclusions from each other. The dimensions of the inclusions are of the order of 1 μm, they differ in composition and magnetic properties, but on average their composition and properties correspond to the ferromagnetic phase $Mn_{1,1}Sb$. At T = 4 K, the crystalline anisotropy of GaSb <Mn> is accompanied by magnetic anisotropy; at T = 300 K, spherical clusters of a magnetic semiconductor retain the properties of a soft magnetic ferromagnet with a coercive force $H_c \approx 10$ E.**

Keywords: **magnetic semiconductors, crystal lattice defects, dislocations**

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Contents

1. INTRODUCTION

To date, it is becoming increasingly apparent that the creation of materials for spin electronics in the form of diluted magnetic semiconductors (DMS) based on III – V semiconductor compounds with a Curie temperature of 300 K and higher is very problematic [1,2]. Doping with *d*-elements of these semiconductors, which have a narrow homogeneity region, leads to the formation of magnetic microinclusions on crystal lattice defects of the synthesized materials. In particular, according to the results of electron probe microanalysis, the textured polycrystals of indium antimonide doped with manganese, InSb<Mn> obtained by quenching of the melt, contained numerous inclusions with an increased content of manganese of 1 μm or less, located both in the grains themselves and at the boundaries [3]. It was found later that the places of accumulation of manganese are the exits of grain-forming dislocations to the surface of the samples and most of it segregates on InSb dislocations [4].

In [5], based on an analysis of the available literature and experimental data, the concept of impurity dislocation magnetism was formulated, according to which the majority of the impurity atoms segregate on the dislocations of the semiconductor crystal lattice, which determines its electrical and magnetic properties. In this work, the task is to find the relationship of the structure and chemical composition of the crystal lattice dislocations of the semiconductor compound GaSb doped with manganese with its magnetic properties.

2. EXPERIMENTAL PROCEDURE

In [6] there was studied ferromagnetism of the GaSb compound semiconductor containing 2% Mn. The starting components used to prepare bulk GaSb<Mn> samples were *p*-type gallium antimonide with a carrier concentration $p = 2.1 \cdot 10^{16}$ cm^{-3} and carrier mobility of $2.5 \cdot 10^3$ cm^2/(Vs) and pure Mn (99.99%).

The starting mixture was heated at a rate of 200 K/h to 1200 K in a silica ampule sealed off under vacuum and holding at this temperature for 24 h. The resultant alloy was quenched in ice water, while the silica ampule was held in a vertical position. For study alloy properties we used powders and polished transverse sections 2×2×5 mm in average dimensions.

All studies were carried out at the facilities of the centre of collective usage of the Kurnakov Institute of General and Inorganic Chemistry RAS.

The phase composition of the samples was determined at room temperature on a Bruker diffractometer in step scan mode (angular range 2θ = 10°–80°, scan step $\Delta 2\theta$ = 0.02°). Using Ni-filtered CuKα radiation (λ = 1.5418 Å), which was decomposed into the $K_{\alpha 1}$ and $K_{\alpha 2}$ components in X-ray diffraction data processing.

The surface of the polished section was examined by scanning electron microscopy on a Carl Zeiss NVision 40 Cross Beam workstation. The magnetic properties of the GaSb (2% Mn) samples were studied at 4 and 300 K in magnetic fields of up to *H* = 50 kOe using a Quantum Design PPMS-9 automated system. The absolute sensitivity in DC- magnetization measurements was $\pm 2.5 \cdot 10^{-5}$ G cm^3.

3. RESULTS AND DISCUSSION

Fig. 1*a* shows the X-ray diffraction pattern of the GaSb powder containing 2% Mn. Moreover, the X-ray diffraction pattern of the powder contains three weak additional reflections, indexed as reflections from the Mn1.1Sb phase, which has a hexagonal structure with unit-cell parameters *a* = 4.157 Å and *c* = 5.757 Å (ICDD PDFcard no. 01-077-8198). The temperature dependence of magnetization for the powder confirms the formation of the ferromagnetic phase Mn1.1Sb with a Curie temperature $T_C \approx 560$ K. The decrease in the lattice parameter a of GaSb<Mn> by 0.016 Å can be due to the quenching-induced compressive stress [6].

Indeed, the difference is an order of magnitude in the coefficients of linear thermal expansion of the synthesized material (LTE GaSb $\alpha = \sim 5 \cdot 10^{-6}$ K^{-1} [7]) and quartz ampoules (TCR $\alpha = \sim 0.5 \cdot 10^{-6}$ K^{-1} [8]) inevitably leads not only to a change in the crystal lattice parameter, but also to the formation of numerous defects in the crystal lattice of the semiconductor.

It was found that if a transverse crystallographic section made of the semicircular part of the obtained ingot had a microcrystal microstructure, then a section made of the cylindrical part of the ingot had the microstructure of a textured

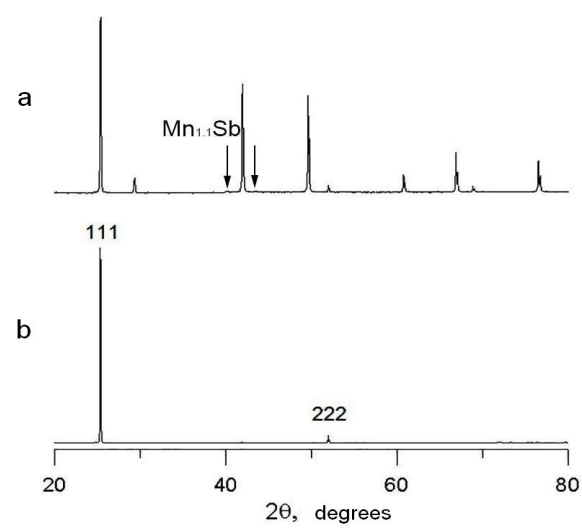

Fig. 1. *X-ray diffraction patterns of the (a) GaSb<Mn> powder and (b) a polished transverse section.*

GaSb (111) polycrystal. The microstructural difference between the transverse sections is a consequence of the vertical position of the ampoule with the melt and radial heat removal at the quenching moment (**Fig. 2***a*).

The formation of a textured polycrystal suggests that grain-forming dislocations are a priority type of defects in the crystal lattice of the cylindrical part of the ingot.

According to [5], this observation is very important, since among other defects of the crystal lattice in III – V semiconductor compounds of the II – V dislocation, due to their exceptional properties — the pronounced anisotropy of the lattice deformation and the ability to segregate impurity atoms on them, occupy a special place.

The segregation of impurities on the dislocation line occurs as follows. In the half-plane zone of the edge dislocation (Fig. 2*b*), the lattice is in a state of excessive hydrostatic pressure, while there is hydrostatic rarefaction on the opposite side of the slip plane [9]. If the crystal is at sufficiently high temperatures, when the mobility of the lattice elements is high, impurity atoms move to these regions of abnormal hydrostatic pressures and impurity atoms accumulate on dislocation lines with the formation of Cottrell clouds [10]. In this case, impurities deposited on the dislocation block its motion, as if "pinning" or, otherwise, fixing the dislocation line at some points [11].

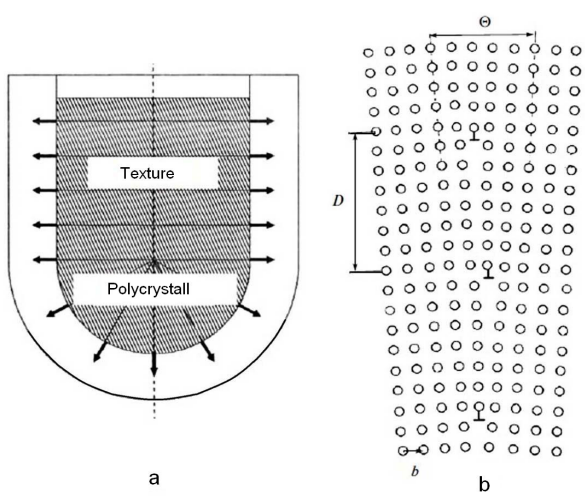

Fig. 2. *Diagram of the position of the ampoule and heat removal from the melt during quenching of GaSb <Mn>(a), leading to the formation of a texture with small-angle boundaries (b).*

According to [9], the boundary between grains is considered small angle if the orientational difference between adjacent sections of the crystal is small. In the simplest case, the grain boundary is constructed from one type of dislocation, for example, only from the edge (Fig. 2*a*). The areas on both sides of the grain boundary are mutually inclined to each other, and the edge of the dihedral angle is located along the grain boundary.

If Θ is the angle of inclination, D is the distance between the exit points of the dislocations and b is the Burgers vector of the dislocation, then for a small angle of inclination we can derive the relation $\Theta = b/D$.

According to the above formula, with constant parameters Θ and b, the distance between the exit points of dislocations D is a strictly constant value. Strict spacing of grain-boundary dislocations ensures strict spacing of segregation points of dopant atoms at dislocations

In our case, from the data of scanning electron microscopy of the surface of a metallographic thin section, it follows that the surface of the GaSb <Mn> magnetic semiconductor consists of microscopic inhomogeneities in the form of etching pits that accumulate in topographic blocks of a triangular shape (**Fig. 3***a*).

According to the results of topographic analysis, microscopic inhomogeneities in the form of straight lines consisting of

etching pits in Fig. 3*a* are slip planes of dislocations. Based on this, it is concluded that the occurrence of linear defects of the crystal lattice - dislocations and their motion during quenching of the gallium antimonide melt doped with manganese are the basis for the formation of the microstructure of the magnetic semiconductor GaSb <Mn>.

The result of scanning the same part of the surface of the sample in X-ray radiation of manganese (Fig. 3*b*) confirms that impurity manganese is mainly contained in these topographic blocks, segregating at dislocations.

Thus, the synthesis of the GaSb <Mn> magnetic semiconductor by quenching of the melt occurs in two stages. At the first stage, dislocations are formed, from which topographic blocks of the microstructure are formed, at the second, impurity manganese fills empty dislocations.

According to published data, dislocation filling of impurity atoms occurs discretely.

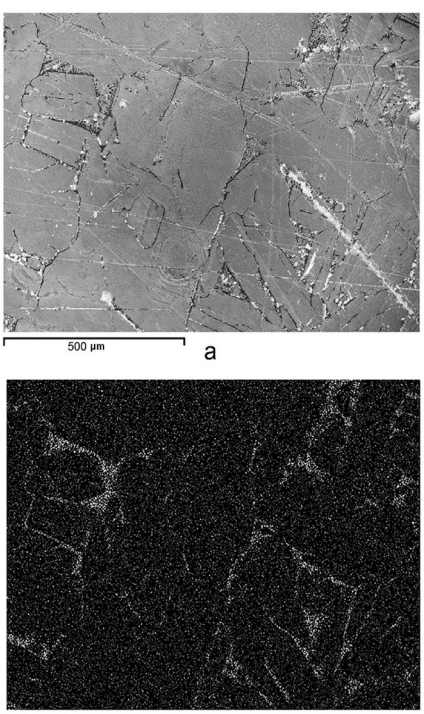

Fig. 3. *Electronic (a) and MnKa (b) X-ray surface topography of a GaSb<Mn> metallographic section.*

For example, in [12], significant deviations from the Cottrell cloud model were observed as a uniform distribution of impurity atoms over cylindrical layers coaxial to the axis of the dislocation. The experimental data [13] also indicate a discrete character of carbon segregation along the dislocation axis in the martensitic alloy with the formation of a chain of segregation atmospheres with a diameter of 14 ± 2 nm (**Fig. 4***a*).

The discrete nature of impurity deposition at dislocations was also noted in earlier studies of dislocations in various materials. For example, in [14], an image of AgCl precipitates on a visually observed spatial dislocation network in a KCl crystal is presented, which is characterized by a surprisingly strict periodic distance between inclusions from each other (Fig. 4*b*). In this case, the sizes of inclusions and the distances between them are the same and amount to 1 μm.

The impurity inclusions of the quenched GaSb <Mn> melt ingot have micron sizes

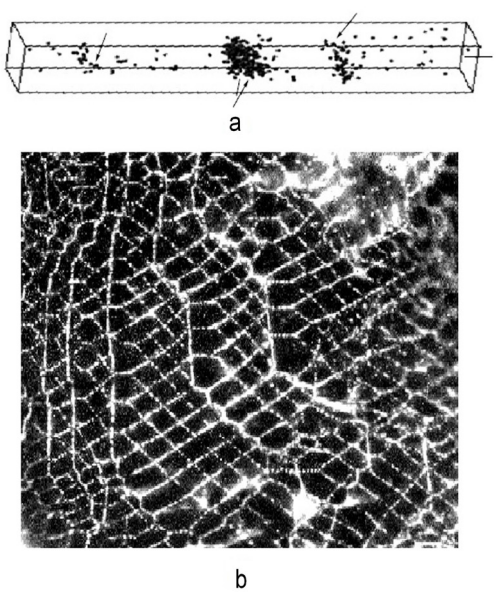

Fig. 4. *Impurity distribution along dislocations: a – distribution of Fe_3C nanoclusters along dislocations in iron (image obtained in an atomic force microscope using a three-dimensional probe); b – precipitates of AgCl on a visually observed spatial dislocation network in a KCl crystal (× 600).*

commensurate with the diameter of the effective region of the X-ray excitation of the electron probe equal to 1 μm [15], which makes it possible to determine the chemical composition in each of the inclusions.

As an example, we consider a chain of microobjects at the small-angle GaSb <Mn> boundary (**Fig. 5***a*). The **Table 1** shows the results of determining the chemical composition of each of the numbered microobjects, from which it follows that microobjects 1-4 are the microinclusions of manganese and antimony, and microobject 5 is an empty dislocation exit to the sample surface. The data of Table 1 were plotted on the lines of magnetic transformations of the Mn-Sb state diagram [16] (Fig. 5*b*), which allowed us not only to carry out phase identification of microinclusions, but also to determine the type of magnetism and Curie temperature of each of them (**Table 2**).

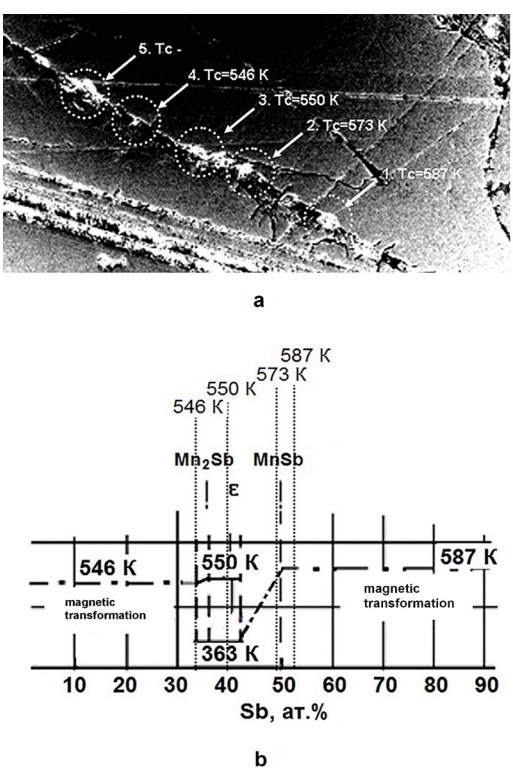

Fig. 5. *Dislocation yields on the GaSb<Mn> surface (×500) (a) and dislocation compositions along the magnetic transformation lines of the Mn–Sb phase diagram (b).*

Table 1

The chemical composition of microinclusions at dislocations

No of inclusion	% at Mn	Ga	Sb
1	48.41		51.59
2	50.52		49.48
3	66.76		33.24
4	62.10		39.90
5		48.22	51.78
1-4	The average composition, at%		
	56.95		43.05

Certain values of the Curie temperature are plotted in Fig. 5*a*. The average Curie temperature of the studied magnetic inclusions is T_C = 564 K and corresponds to T_C = ~ 560 K [6].

Studies at T = 4 K showed the dependence of the magnetization of the metallographic thin section GaSb <Mn> on the angle of its rotation to the direction of magnetic flux and its practical absence at T = 300 K (**Fig. 6***a*).

According to Fig. 6a, it is concluded that, at low temperatures, the crystalline anisotropy of the sample is accompanied by its magnetic anisotropy, caused by the ordered arrangement of magnetic clusters on dislocations in the crystallographic directions <110>.

A decrease in the magnetic anisotropy of the sample with increasing temperature is associated with the destruction of the ferromagnetism of small clusters by thermal

Table2

Curie temperature and type of magnetism of microinclusions at dislocations

No of inclusion	Curie temperature T_c, K	Type of magnetism
1	587	ferromagnet
2	573	ferromagnet
3	550	ferromagnet
4	546	ferromagnet
5	-	diamagnet
Average	564	ferro-/ferrimagnet

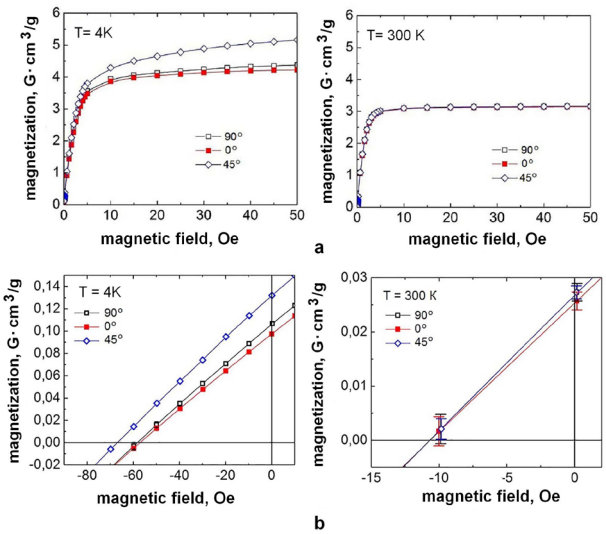

Fig. 6. *Magnetic field dependences of magnetization (a) and coercive force (b) for a polished transverse section of GaSb <Mn> as a function of rotation angle at T = 4 and 300 K.*

vibrations of atoms as they approach the superparamagnetic state.

The measurements of magnetic properties showed that, at a temperature of T = 300 K, the GaSb <Mn> sample still retains the properties of a ferromagnet with a coercive force of the soft magnetic material $H_C \approx 10$ Oe (Fig. 6b).

This is also confirmed by the results of calculations in [6], in which, based on measurements of magnetization after cooling without a field (ZFC) and cooling in a field (FC), it was concluded that ferromagnetic microinclusions at room temperature are close to a superparamagnetic state with a blocking temperature of magnetic moments of ferromagnetic clusters $T \approx 300$ K. The calculated effective size of the blocked clusters is ≈ 200 nm, which is several times smaller than the average size of the observed magnetic microinclusions at dislocations.

The **Fig. 7***a* shows a portion of the surface of a sample with a horizontal exit to the surface of a mixed linear screw dislocation with several spherical clusters and a diagram of a rectangular hysteresis loop of an

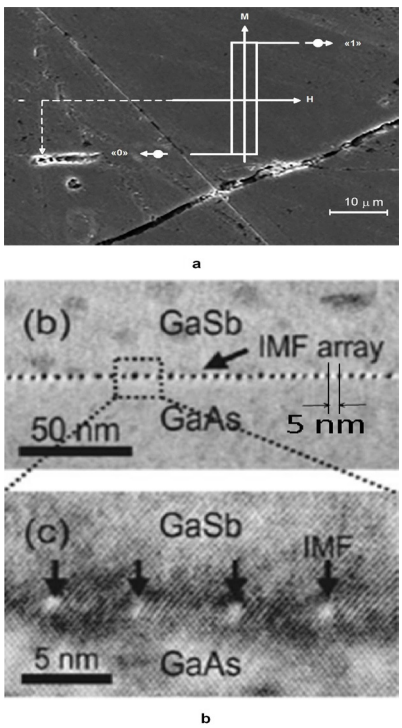

Fig. 7. *Possible applications of segregation of magnetic impurities on dislocations: a - spherical clusters at the horizontal dislocation exit to the surface of the GaSb <Mn> sample and the scheme of the hysteresis loop of the information bit on one of them; b — mismatch dislocations at the GaSb / GaAs heteroboundary according to* [17].

information bit on one of them. Therefore, spherical clusters at dislocations can be used as bits of information in computer random access memory.

The integration of magnetic systems into semiconductor electronics involves the fusion of layers of semiconductors of the same syngony with different structural parameters and, as a result, the formation of a misfit dislocation layer between them (Fig. 7*b*) [17,18].

By varying the structural parameters of semiconductors, the concentration of the alloying element, and the conditions for obtaining, it is possible to create mismatched base elements of magnetoresistive random access memory (MRAM) of various sizes and densities on dislocations.

4. CONCLUSIONS

It was found that quenching of the GaSb<Mn> melt in water at a vertical location of the ampoule, radial heat removal, and the difference in the thermal expansion coefficient of the synthesized material and quartz leads to the formation of (111) GaSb texture and is an effective method for generating high-density grain-forming dislocations.

Manganese atoms segregate on GaSb dislocations discretely with periodic spacing of inclusions from each other. The size of the inclusions is about 1 μm.

According to the microanalysis data, inclusions at dislocations differ in composition and magnetic properties, but the total composition is close to the $GaSb_{1,1}Mn$ phase observed by the XRD method, and the average Curie temperature of microinclusions corresponds to T_C ~ 560 K, determined as a result of GaSb<Mn> magnetic measurements.

The micron sizes of inclusions on dislocations bring their ferromagnetic state closer to the superparamagnetic state and cause magnetic anisotropy at low temperatures.

At room temperature, GaSb<Mn> retains the properties of a ferromagnet with a coercive force of soft magnetic material $H_C \approx 10$ Oe. Microswitches on dislocations can be used as bits of information in computer random access memory.

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